New Far Infrared Vibrational Mode in Zn Doped CuGeO₃

J. J. McGuire[1], T. Rõõm[1,a], T. E. Mason[2], T. Timusk[1]

[1] *Department of Physics and Astronomy, McMaster University, Hamilton, Ontario L8S 4M1, Canada*
[2] *Department of Physics, University of Toronto, Ontario M5S 1A7, Canada*

H. Dabkowska

Brockhouse Institute for Materials Research, McMaster University, Hamilton, Ontario L8S 4M1, Canada

S. M. Coad, D. McK. Paul

Department of Physics, University of Warwick, Coventry CV4 7AL, UK
(June 24, 1997, submitted to Phys. Rev. Lett.)

We report on far infrared measurements on Zn and Si doped crystals of the spin-Peierls compound CuGeO₃. Zn doping has the effect of introducing several new absorption lines, polarized in the ab-plane, between 5 and 55 cm⁻¹. The intensity of the absorption grows with Zn concentration but saturates above 2 % Zn. One line at 10 cm⁻¹ loses intensity above 4 K, and a second line at 20 cm⁻¹ is absent at low temperatures but grows to peak at about 40 K in agreement with a three level model with two excited states 10 and 30 cm⁻¹ above the ground state. As the doping is increased these lines broaden, and a temperature independent absorption develops over the entire range from 5 to 55 cm⁻¹. These features are magnetic field independent up to 16 T and are absent in Si doped samples. We suggest the new absorption is due to localized lattice modes of the zinc ion and the surrounding GeO₄ tetrahedra.

PACS numbers: 75.50.Ee, 78.30.Hv, 63.20.Pw

The quasi-one-dimensional antiferromagnet CuGeO₃ is the first inorganic compound to show a spin-Peierls (SP) transition [1]. At $T = 14$ K a gap opens in the excitation spectrum of the Cu $S = \frac{1}{2}$ spins as a result of magneto-elastic coupling. In general, such transitions involve a lowering of magnetic energy at the expense of lattice energy. Structures where large tightly bound blocks can move as units, such as the organic charge transfer complexes, exhibit the spin-Peierls phenomenon. Similar structural units occur in oxides in the form of rigid GeO₄ or SiO₄ tetrahedra bonded weakly to each other to form easily distorted structures [2]. It has been found that in CuGeO₃ the SP transition involves both a dimerization of the copper ions along the **c**-axis and a rotation of the GeO₄ tetrahedra about the **c**-axis [3]. In this paper we present the results of a far infrared transmission study of Zn and Si doped CuGeO₃. Our results show that Zn substitution for Cu induces new absorption lines at 10 and 20 cm⁻¹. We show that these transitions result from a very unusual, highly anharmonic localized vibrational mode.

The lattice structure of CuGeO₃ is shown in Fig. 1. It consists of chains of relatively rigid GeO₄ tetrahedra along the **c**-axis. Cu²⁺ ions are positioned between these chains and form chains of CuO₆ octahedra which share the GeO₄ oxygens. Adjacent octahedra share two oxygens which provide a superexchange path for the antiferromagnetic interaction between Cu²⁺ ions.

The far infrared absorption spectrum of pure CuGeO₃ has a weak absorption line in the SP phase at 44 cm⁻¹ [4] which corresponds to the SP gap energy (≈ 5.5 meV) at $\mathbf{Q} = [0,0,0]$ of the magnetic Brillouin zone as determined
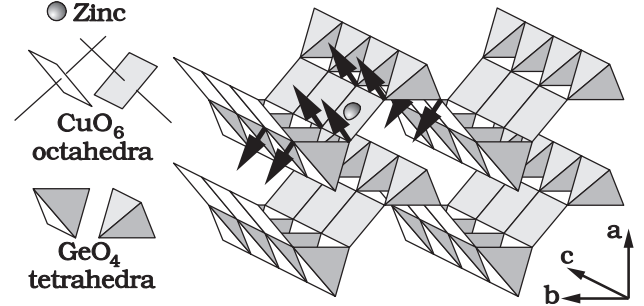

FIG. 1. Lattice structure of CuGeO₃. Arrows show possible motion of the rigid GeO₄ tetrahedra ascociated with a Zn-induced local vibrational mode.

by electron spin resonance [5]. The line splits in a magnetic field as expected for a transition from the ground singlet state to the excited triplet state. The other low-lying spectral feature is a weak phonon at 48 cm⁻¹ suggested to correspond to a displacement of the four planar oxygens in the direction of the apical oxygens in the CuO₆ octahedra [6].

Doping of CuGeO₃ with Zn or Si is particularly interesting because it results in an antiferromagnetic (AF) phase that seems to coexist with the SP phase in a range of temperatures and doping levels in Cu₁₋ₓZnₓGeO₃ [7–11] and in CuGe₁₋ₓSiₓO₃ [12–14]. There are, to our knowledge, no measurements of the far infrared spectrum of the doped systems of CuGeO₃.

We studied several single crystals including an undoped sample, a Si doped sample with $x = 0.003$, and a series of Zn doped samples with $x = 0.003, 0.01, 0.02$

and 0.05. The Néel and SP transition temperatures, T_N and T_{SP}, were determined from magnetic susceptibility measurements on the same crystals. The $x = 0.01$, 0.02 and undoped samples were grown by a floating zone technique and the $x = 0.003$ and 0.05 samples by a self flux method. We used either atomic emission spectroscopy or mass spectroscopy to determine the Zn and Si concentrations and found good agreement with phase diagrams [8,11,12] for T_{SP} and T_N *vs.* concentration x.

The far infrared measurements were done with a home-built polarizing Fourier spectrometer [15] and a new magnet insert with an *in situ* ^{3}He cooled ($T = 0.3$ K) silicon bolometer. Polarization-dependent transmission measurements were done in magnetic fields up to 16 T from 3 to 100 cm^{-1} and in the temperature range from 1.2 to 100 K. Sample sizes were about $0.6 \times 2.5 \times 4$ mm^3 in the directions of the **a**, **b** and **c** crystallographic axes [16] respectively. The **k**-vector of the light was aligned along the **a**-axis (**k**∥**a**). To establish the symmetry of the transitions, additional measurements were done with **k**∥**b** for one of the Zn doped samples ($x = 0.01$). The dc magnetic field was in the direction of light propagation (Faraday geometry), and most of the spectra were measured at 1 cm^{-1} resolution. To calculate the absorption coefficient α from the transmittance it is necessary to estimate the refractive index. We used the interference fringes from a thin sample with parallel faces to do this. A constant value of $n = 3$ was determined for the entire range from 3 to 100 cm^{-1}.

The absorption spectra for several samples at 1.2 K are shown in Fig. 2. The sample doped with $x = 0.003$ Si is very similar to the undoped sample (not shown) in that the only far infrared features are the line at 48 cm^{-1} which has been identified as a B_{3u} phonon [6], and the shoulder at 44 cm^{-1} due to the singlet to triplet transition [4]. In contrast, the $x = 0.003$ Zn sample shows, in addition to these features, a line at 10 cm^{-1} which is not present in the Si doped sample (or in the undoped samples). Increased doping results in a broadening of the 10 cm^{-1} line and the development of a broad absorption band between 5 and 55 cm^{-1}. The variation of the spectral weight [17] from 3 to 60 cm^{-1} (background and phonon line subtracted) is shown in the inset to Fig. 2 as a function of concentration. The dependence on Zn concentration appears to be linear at low concentrations but quickly saturates above $x = 0.02$.

Absorption spectra for the $x = 0.003$ Zn doped sample were also obtained at higher temperatures. While the shoulder at 44 cm^{-1} disappears above the SP transition temperature as expected, the 10 cm^{-1} line and another line at 20 cm^{-1} show a temperature dependence that has no obvious relationship to the SP transition. The spectra are shown in the upper panel of Fig. 3, and the lower panel shows the spectral weight of the 10 and 20 cm^{-1} lines as functions of temperature. The 10 cm^{-1} line loses intensity as temperature is increased, but the 20 cm^{-1}
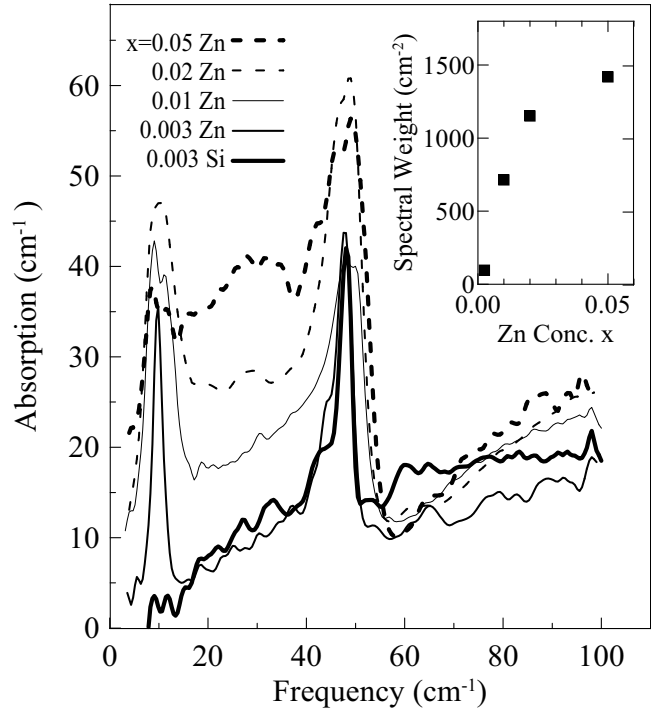

FIG. 2. Doping dependence of far infrared absorption of CuGeO$_3$ crystals at 2 K with b-polarization and **k**∥**a**. The inset shows spectral weight from 3 to 60 cm^{-1} as a function of Zn concentration. The spectral weight does not include the background which is taken to be the Si doped sample spectrum.

line, which is absent at low temperatures, grows in intensity to peak around 40 K. Both lines shift to higher frequencies with temperature (inset to Fig. 3), and the 20 cm^{-1} line broadens significantly. Although the 10 and 20 cm^{-1} lines are broader in the more highly doped samples, they still show this temperature dependence. The broad absorption from 5 to 55 cm^{-1} in samples with $x > 0.003$ is temperature independent up to 100 K.

The temperature dependence of the 20 cm^{-1} line suggests that it is a transition from an excited state. A simple three level model with two excited states 10 and 30 cm^{-1} above the ground state accounts for the temperature dependences of the line intensities in the lower panel of Fig. 3. The trends in the data are correctly reproduced, and the quality of the fit, though not particularly good, can be improved by adding higher energy levels to the model. This points to a multilevel, very anharmonic excitation, which is made possible by the replacement of a Cu^{2+} ion with Zn^{2+}, but not by the substitution of Si for Ge.

The polarization dependence of the new features was also obtained. With **k**∥**a**, the 10 and 20 cm^{-1} lines as well as the 5 to 55 cm^{-1} band were strongest when the electric field was along the **b**-axis (b-polarization) and nearly ab-
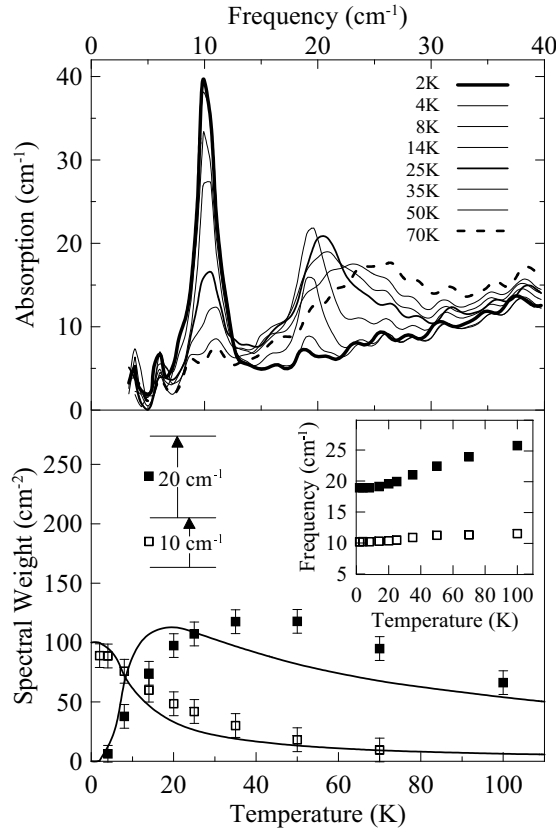
FIG. 3. Temperature dependence of 10 and 20 cm^{-1} lines in the $x = 0.003$ Zn doped sample. The upper panel shows absorption at various temperatures with b-polarization and $\mathbf{k}\|\mathbf{a}$. The lower panel shows the spectral weight of the lines calculated using Lorentzian fits with frequencies shown in the inset. Solid lines are fits to the simple three-level model: $I_{10}(T) = A_{10}(1-e^{-\Delta_{10}\beta})/(1+e^{-\Delta_{10}\beta}+e^{-(\Delta_{10}+\Delta_{20})\beta})$, $I_{20}(T) = A_{20}e^{-\Delta_{10}\beta}(1-e^{-\Delta_{20}\beta})/(1+e^{-\Delta_{10}\beta}+e^{-(\Delta_{10}+\Delta_{20})\beta})$, where Δ_{10} and Δ_{20} are the temperature dependent transition frequencies (inset), $A_{10} = 100$ and $A_{20} = 500$ are adjustable parameters, and $\beta = (k_B T)^{-1}$.

sent with c-polarization. When the $x = 0.01$ Zn sample was oriented with $\mathbf{k}\|\mathbf{b}$, the features were strongest with a-polarization. Thus, if these are magnetic dipole transitions, they require that the magnetic field component of the light is along the $\mathbf{c}$-axis. If they are electric dipole transitions, the electric field must be in the ab-plane and have components both in the $\mathbf{a}$ and $\mathbf{b}$ directions.

To exclude magnetic dipole transitions we compare the spectral weight of the Zn-induced absorption with that of a known magnetic dipole transition in our system. An incommensurate phase exists in $CuGeO_3$ above $B_0 \approx 12$ T [18,19] where a magnetic dipole transition in the triplet ground state can be observed [4]. We find this transition (at 15 cm^{-1} in Fig. 4) to be independent of polarization in the bc-plane ($B_0 = 15$ T along the $\mathbf{a}$-axis)
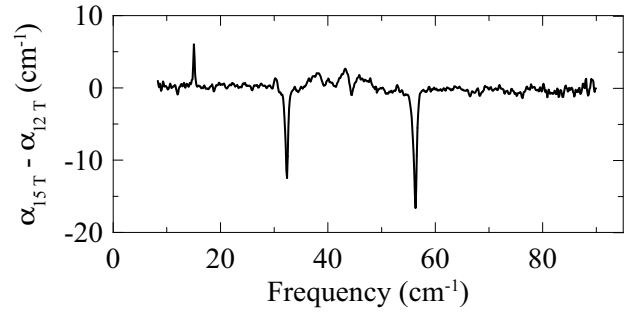

FIG. 4. Absorption in the SP phase at 12 T (negative features) subtracted from absorption in the incommensurate phase at 15 T (positive features) for the undoped sample at 2.1 K and 0.2 cm^{-1} resolution with b-polarization and $\mathbf{k}\|\mathbf{a}$.

as expected for an $S = 1$, $\Delta M = \pm 1$ transition and to have a spectral weight of 2.5 cm^{-2}. The spectral weight of the 10 cm^{-1} line is 100 cm^{-2}, a factor of 40 larger than the magnetic dipole transition. This discrepancy, which is even larger if we include the dilution due to low Zn concentration, in combination with the fact that the frequency of the Zn-induced absorption is not affected by magnetic field up to 16 T, leads us to conclude that it is not a magnetic dipole transition.

We can also rule out forbidden electronic electric dipole transitions such as the transition in the SP phase from the singlet ground state to the excited triplet state which produces the 44 cm^{-1} line. That line splits in a magnetic field as shown in Fig. 4 due to the splitting of the excited triplet state. It is also ten times stronger than the magnetic dipole transition at 15 cm^{-1}, and as our study has shown, is induced when $\mathbf{k}\|\mathbf{a}$ with b-polarization only. If the Zn induced features are electronic electric dipole transitions, it is unclear which states could be involved. Since they are not split by a magnetic field, they are unlikely to involve transitions to or from triplet states. In-gap states, predicted by Martins $et\ al.$ [20], are also excluded because they would be absent above the SP transition temperature.

Local vibronic modes are another possibility. For a pure Zn translational mode for $x = 0.003$ Zn we estimate a spectral weight of 530 cm^{-2} from the plasma frequency $\omega_p = (4\pi n Z^2 e^2/M)^{1/2} = 13$ cm^{-1} where n is the Zn concentration, M the mass of the Zn ion and Z the effective charge which we take to be $+2$. This is over 5 times larger than the observed spectral weight. It is therefore likely that the mode also involves motion of other atoms.

The three level system shown in Fig. 3 can be modeled with a square well with a central barrier. Appropriate choice of parameters gives levels at 10, 30 and 55 cm^{-1}. Electric dipole transitions between levels of opposite parity will give lines at 10, 20, 25 and 55 cm^{-1}. The line at 25 cm^{-1} is weak at the temperatures investigated because the population of the 30 cm^{-1} level is small, and

the 55 cm^{-1} line is weak because of the small transition matrix element from the ground state to the 55 cm^{-1} level. In general, the addition of the level at 55 cm^{-1} will improve the agreement between the calculated and observed temperature dependance of the line intensities shown in lower panel of Fig 3. The broadening of the 10 and 20 cm^{-1} lines with increased doping can be explained as being due to long range of interaction between the defects.

The combination of a low intensity, a flat very anharmonic potential and a polarization in the *ab*-plane suggests that the lines at 10 and 20 cm^{-1} involve the Zn defect and the libration about the **c**-axis of the surrounding four GeO$_4$ tetrahedra as shown in Fig. 1. In the undoped material the 48 cm^{-1} phonon is a similar mode which is optically active [6] and involves the motion of the Cu in the direction of the apical oxygens. With Cu replaced by Zn this mode would have a polarization with both **a** and **b** direction components and is consistent with the model of a potential well with a central barrier. Since Zn is known to favor a higher coordination number than Cu it will have a tendency to move off center towards one of the apical oxygens.

Libration of GeO$_4$ tetrahedra is also a component of the *static* SP distortion in the undoped material [3,21], but it is not optically active since it involves odd combinations of the rotations of the GeO$_4$ tetrahdra and no displacment of the copper in the *ab*-plane. In our picture the Zn doping has the effect of moving the mode at 48 cm^{-1} to 10 cm^{-1} by a dramatic reduction of the already weak restoring force for diplacements of the the planar oxygens in the direction of the apical oxygens around the Zn.

In contrast to the large changes in dynamics by Zn doping, the replacement of Ge by Si will have the minor effect of reducing the size of one of the tetrahedra affecting four Cu sites equally and, by symmetry, giving rise to a low frequency optical mode polarized in the **b** direction. We have not observed such a mode in our Si doped samples from 3 to 100 cm^{-1}.

One feature which remains to be explained is the 5 to 55 cm^{-1} band seen at higher doping levels. Its lower boundary is approximately defined by the 10 cm^{-1} line, and the upper boundary more or less coincides with the phonon at 48 cm^{-1}. The saturation of the absorption above a concentration of $x = 0.02$ (inset to Fig. 2) is reminiscent of the phase diagram [8,11] in which T_N and T_{SP} stop changing at this same concentration. This may be evidence for an upper limit for effective doping. Another possibility, suggested by the unusual flat shape of the band, is that it represents a disordered state of the local excitations as they begin to interact strongly at $x = 0.02$ Zn and above. This state may also be relevant to the saturation of T_N and T_{SP} at the same doping level.

In summary we have observed a low lying lattice mode in Zn doped CuGeO$_3$ which we idenify with the librational motion of GeO$_4$ tetrahedra combined with the dis-placment of Zn in a very flat potential with a central barrier.

[a] Permanent address: Institute of Chemical Physics and Biophysics, Akadeemia tee 23, Tallinn EE0026, Estonia.
[1] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993).
[2] K. D. Hammond, H. Deng, V. Heine, and M. T. Dove, Phys. Rev. Lett. **78**, 3701 (1997).
[3] K. Hirota *et al.*, Phys. Rev. Lett. **73**, 736 (1994).
[4] P. H. M. van Loosdrecht *et al.*, Phys. Rev. B **54**, R3730 (1996).
[5] T. M. Brill *et al.*, Phys. Rev. Lett. **73**, 1545 (1994).
[6] Z. V. Popović *et al.*, Phys. Rev. B **52**, 4185 (1995).
[7] J. G. Lussier, S. M. Coad, D. F. McMorrow, and D. McK. Paul, J. Phys.-Cond. Matter **7**, L325 (1995).
[8] Y. Sasago *et al.*, Phys. Rev. B **54**, R6835 (1996).
[9] M. Hase *et al.*, J. Phys. Soc. Jpn. **65**, 1392 (1996).
[10] P. Fronzes, M. Poirier, A. Revcolevschi, and G. Dhalenne, Phys. Rev. B **55**, 8324 (1995).
[11] M. C. Martin *et al.*, Phys. Rev. B submitted (1997).
[12] J. P. Renard *et al.*, Europhys. Lett. **30**, 475 (1995).
[13] L. P. Regnault, J. P. Renard, G. Dhalenne, and A. Revcolevschi, Europhys. Lett. **32**, 579 (1995).
[14] M. Poirier *et al.*, Phys. Rev. B **52**, R6971 (1995).
[15] Design of the far infrared spectrometer will be published later.
[16] H. Völlenkle, A. Wittmann, and H. Nowotny, Monatsh. Chem. **98**, 1352 (1967).
[17] We define spectral weight (in units of cm^{-2}) as $\int_0^\infty \alpha d\nu = (\pi^2/n)\omega_p^2$ where the absorption constant α, the frequency ν and the plasma frequency ω_p are in units of cm^{-1} and n is the index of refraction.
[18] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. B **48**, 9616 (1993).
[19] V. Kiryukhin *et al.*, Phys. Rev. B **54**, 7269 (1996).
[20] G. B. Martins, E. Dagotto, and J. Riera, Phys. Rev. B **54**, 16032 (1996).
[21] M. Braden *et al.*, Phys. Rev. B **54**, 1105 (1996).